Damage induced by plasma etching: On the correlation of results from photoluminescence and transport characterization techniques

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(Received 27 June 1994; accepted for publication 3 January 1995)

Plasma dry etching, used for the fabrication of low-dimensional structures, is known to create defects in the material which affect both the optical and the transport properties of the sample. We compare the results obtained from three different methods of characterizing the damage induced by electron cyclotron resonance metalorganic reactive ion etching to the two-dimensional electron gas (2DEG) in GaAs/AlGaAs heterostructures: photoluminescence, transport measurements, and electron paramagnetic resonance. Etching impairs the quality of luminescence and decreases the single-particle relaxation time, while the concentration of a surface related paramagnetic defect (probably dangling bonds) is increased. However, detailed experiments show no correlation between the density of defects and transport or luminescence properties, nor between transport and luminescence properties. In particular, hydrogen passivation, which improves the luminescence properties after etching, leads to deteriorated transport properties. © *1995 American Institute of Physics.*

Dry etching methods are important techniques for the patterning of low-dimensional systems in multilayer semiconductor structures. Their main advantages are their high anisotropy, uniformity, and very well controllable etch rate.[1–3] However, dry etching is known to create defects in the material that can degrade the transport and photoluminescence properties of the sample.[1,2] In order to optimize the etching parameters in terms of low damage, an efficient technique for the characterization of the damage is required. Several different methods to characterize the sample can be used. Transport measurements, for instance, give information on the electron scattering probability and the number of free carriers. Electron paramagnetic resonance (EPR) gives the total density of paramagnetic defects. The photoluminescence (PL) of a multilayer structure degrades when recombination centers or inhomogeneities are introduced. Since each technique is sensitive to different properties, there is an obvious risk of optimizing inappropriate sample parameters for a specific application, when the wrong technique is used. In this letter, we present a comparative investigation of the three techniques mentioned above. The surface of GaAs/AlGaAs heterostructure samples containing a high mobility, two-dimensional electron gas (2DEG) has been etched using electron cyclotron resonance metalorganic reactive ion etching (ECR-MORIE). We compare the changes in the properties of the sample as characterized by PL and EPR with the behavior of the single-particle relaxation time τ_s and the carrier concentration as obtained from Shubnikov–de Haas (SdH) oscillations detected by microwaves. In a number of experiments, including wet etching, hydrogen passivation, and annealing, the correlation of changes in the different properties of the sample is investigated.

We used modulation-doped 2DEG GaAs/$Al_xGa_{1-x}As$ ($x=0.3$) structures grown by metalorganic vapor phase epitaxy (MOVPE). The heterostructure consisted of an 800 nm, undoped GaAs layer, a 15 nm, undoped $Al_{0.3}Ga_{0.7}As$ layer, a 70 nm, Si-doped ($5–10\times10^{17}$ cm^{-3}) $Al_{0.3}Ga_{0.7}As$ layer and a 20 nm, 5×10^{16} cm^{-3} Si-doped GaAs capping layer. The pieces used in the experiments were about 2×4 mm^2 in size.

For both transport and EPR measurements, a Bruker ESP 300 spectrometer, working at 9.5 GHz microwave frequency was used. All measurements were made at $T=4.2$ K. For SdH experiments, the sample is placed in the resonator of the spectrometer, and oscillations are detected as changes in the microwave conductivity.[4] For the determination of the single-particle relaxation time[5,6] τ_s we measured the magnetic field B at the onset of the SdH oscillations. SdH oscillations can be resolved when the relation $\omega_c\tau_s\geqslant1$ is fulfilled, where $\omega_c=eB/m^*$. Using our detection technique at a temperature of 4.2 K, we determined, in a calibration experiment, $\omega_c\tau_s=0.7$ at the onset of oscillations, and can in this way determine τ_s for other samples. The mobility of the untreated material was about 9.5 m^2/V s, the single-particle relaxation time varied for the different pieces between 0.5 and 0.7 ps, and the carrier concentration varied between 6.2 and 6.9×10^{11} cm^{-2}.

In EPR measurements, in some of the untreated pieces a single, isotropic line, denoted DB, was detected. The Zeeman splitting factor was $g=2.0$ and the linewidth 10–12 G. The DB concentration in the untreated samples was of the order of the detection limit of 10^{11} cm^{-2}. The defect is not identified, but the results given below strongly indicate that it is located at the surface or very close to it. Tentatively, we attribute it to a dangling bond at the surface.

For optical characterization we used a low temperature (5–7 K), optical fiber PL setup with a 488 nm cw Ar^+ ion laser that resulted in an excitation power density of the order of 10 W/cm^2. A PL spectrum of an untreated sample is

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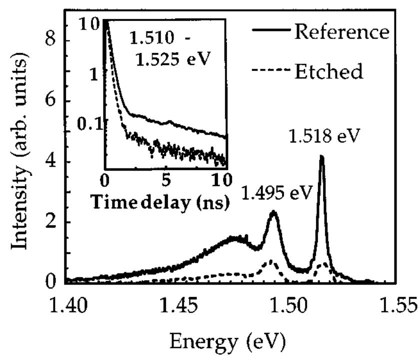

FIG. 1. PL of a GaAs/AlGaAs heterostructure before (full line) and after (dashed line) ECR-MORIE etching. In the insert the time-resolved PL of the energy range between 1.510 and 1.525 eV is shown, where the fast contribution to the PL of the etched sample (dashed line) is normalized to the value of the unetched sample (full line).

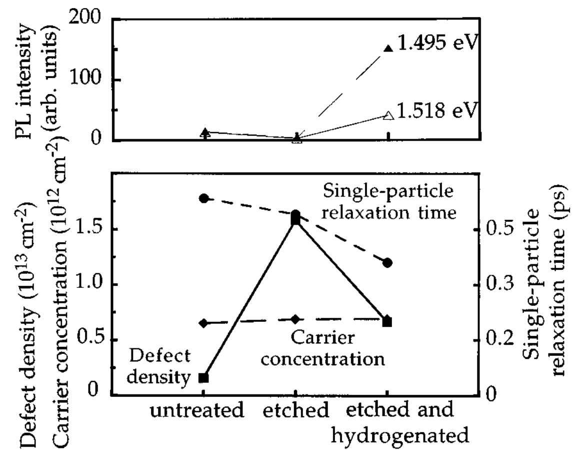

FIG. 2. The behavior of the PL intensity, the paramagnetic defect density, the single-particle relaxation time and the carrier concentration after dry etching of 10 nm of the cap GaAs layer and subsequent hydrogen passivation.

shown in Fig. 1. Two strong lines were detected, one at 1.495 eV, another at 1.518 eV, together with a broad line at about 1.48 eV. For a better understanding of the spectrum, we carried out time-resolved PL measurements with 40 ps pulses from a 655 nm laser diode and a C4334 Hamamatsu streakscope for the analysis of the emitted light. As shown in the inset of Fig. 1, the 1.518 eV line can be resolved in time into two contributions, one with a decay time of 0.3 ns, and a slower one with a decay time of 8 ns. We attribute the fast contribution to excitonic recombinations in the bulk GaAs, the slower to transitions of electrons in the 2DEG to free holes in the GaAs.[7–9] The time dependence of the 1.518 eV line is thus an instrument to study the damage caused by surface treatments, since the contribution from the 2DEG will be relatively more sensitive than the contribution from the bulk. The 1.495 eV line is due to bulk donor–acceptor pair (DAP) recombination.[7–9]

Plasma dry etching was done in an ECR-MORIE reactor.[10] The flow rates of H_2, CH_4, and Ar were 3.0, 1.6, and 1.2 sccm, respectively, the pressure in the chamber was 1.5 mTorr. During etching, the sample was biased at 90 V and reached an estimated temperature of less than 60 °C. Under these conditions, about half of the 20 nm GaAs cap layer was etched off at an etching rate of 1.6 nm/min.

The impact of the etching on a typical sample is illustrated in Fig. 2. The single-particle relaxation time is usually decreased by 10%–20%, but decreases by up to 50% have been observed. The carrier concentration does not change significantly, while the DB concentration increases by at least a factor of 10, in some samples even values of 2×10^{14} cm^{-2} have been obtained. It is important to characterize the samples immediately after etching, because we found that the DB concentration decreased by approximately 30% within the first 6 h, independent of whether the sample was stored at room temperature or at 77 K. As shown in Fig. 1, the intensity of all PL lines decreases with a simultaneous increase of the linewidth. The 1.518 eV line is relatively more affected than the 1.495 eV line, which can be understood with the help of the normalized, time-resolved PL of the high energy line after etching (inset of Fig. 1). The decay times are only slightly changed, but the intensity of the slower 2DEG—free hole contribution is more reduced than that of the bulk excitonic contribution. This result clearly shows that the etching process used in this work causes damage in the 2DEG region, which is sensed by PL.

Hydrogen passivation is known to improve the PL properties of GaAs considerably.[11] Hydrogenation was done in the MORIE chamber for 60 min at 200 °C, but without biasing the sample. As shown in Fig. 2, both PL lines show strongly increased intensity after passivation. The 1.495 line is increased by a factor of 40, and the 1.518 eV line by a factor of 14. However, these improvements of the PL signal are not reflected in the transport properties. In fact, the single-particle relaxation time decreased even further, while the carrier concentration remained the same. To find out about the role of hydrogenation in the scattering probability, a sample was hydrogenated at 200 °C without prior etching. Again, the PL intensity increased, while the single-particle relaxation time decreased, in this case, by 25%. The treatment caused also a decrease of the carrier concentration by about 60%. These results show that, if hydrogen is involved, the PL signal cannot be used to judge the quality of the sample for transport experiments. The reduction of the single-particle relaxation time is an effect of the exposure to a hydrogen-containing plasma and not of the etching process itself. UV radiation from the ECR plasma or diffusion of atomic hydrogen into the sample might be responsible for this behavior. Heating of untreated samples in vacuum causes no observable changes.

It is known that chlorine-based dry etching techniques usually lead to a reduced value of the carrier concentration.[12] ECR-MORIE dry etching, under the conditions used by us, does not change the carrier concentration, neither does hydrogenation after etching. The reason for the discrepancy between these results and the fact that hydrogenation without preceding etching repeatably reduced the carrier concentration strongly, has not been clarified.

The DB density, as measured by EPR, decreased upon hydrogenation passivation together with the improvement of the PL signal. To find out more about the origin of the DB signal and its role for transport and PL properties, we carried out wet etching experiments. A mixture of

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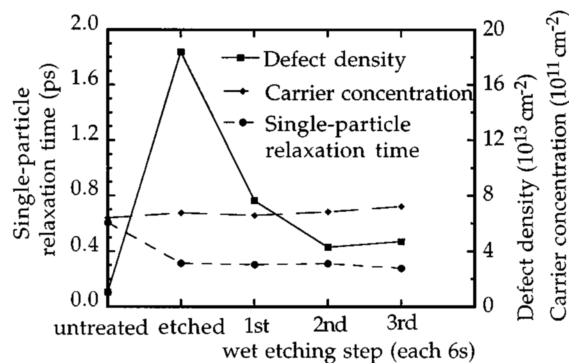

FIG. 3. The single-particle relaxation time, the carrier concentration, and the paramagnetic defect density after 10 s of dry etching and three subsequent wet etching steps, each lasting for 6 s. The defect density is decreased while the other two properties remain unchanged.

$H_3PO_4:H_2O_2:H_2O$ (3:1:50) etches GaAs at a rate of about 1.5 nm/s at room temperature.[12] After dry etching of 10 nm of the GaAs cap layer and characterization, most of the remaining 10 nm were removed by 6 s of wet etching. The results are shown in Fig. 3. As usual, the carrier concentration remained unchanged upon dry etching, while the single-particle relaxation time decreased and the DB concentration increased. The removal of the surface layer by wet etching decreased the DB density by more than a factor of 2. A second and third wet etching step reduced the DB concentration even further. The defects are obviously located close to the surface, which enables us to interpret them as dangling bonds. Remarkably, the scattering probability as expressed by τ_s and the carrier concentration did not change during the whole experiment.[13] This is a strong indication that the increased scattering probability of the 2DEG electrons upon etching is not caused by the defects detected in EPR.

After annealing of an etched sample for 15 min in vacuum, we found that the DB concentration varied strongly upon heating at different temperatures up to 380 °C, while none of the other properties of the sample exhibited significant changes. This confirms once more that the paramagnetic defects affect neither the luminescence nor the transport properties.

To summarize, we have investigated the damage caused by ECR-MORIE to the 2DEG in GaAs/AlGaAs heterostructures. We have compared the results obtained from photoluminescence, Shubnikov–de Haas oscillations, and electron paramagnetic resonance. We found that the concentration of a paramagnetic surface defect, which we attribute to dangling bonds, neither correlates with the quality of luminescence nor with the transport properties of the sample. Furthermore, optical and transport properties are not directly related to each other. In particular, hydrogen passivation, which leads to a substantial improvement of the PL properties, causes a clear increase of the scattering probability in the 2DEG. PL characterization cannot be used in this case to judge the suitability of a sample for transport applications.

This work was performed within the ''nanometer structure'' Consortium in Lund and was supported by the Swedish Natural Science Research Council and the Swedish Research Council for Engineering Sciences. The authors thank the Epitaxial Laboratory at the Institute of Microelectronics Technology, Chernogolovka, Russia for supplying an ECR-plasma source.

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[13] Subsequent etching of in total more than 18 s of other samples, deep enough to remove part of the doping layer, resulted in the decrease of the carrier concentration followed by the disappearance of the SdH oscillations due to low mobility.

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